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On-Site Analysis of Explosives in Soil

Evaluation of Thin-Layer Chromatography for Confirmation of Analyte Identity

Sae-Im Nam

August 1997

Abstract: Two colorimetric-based methods are commonly used for on-site analysis of explosives in soil. For the TNT method, acetone soil extracts are reacted with base to produce reddish-colored Janowsky ions. For RDX, acetone extracts are acidified and reacted with zinc to reduce RDX to nitrous acid, and the nitrous acid is determined by reacting the resulting solution with a Griess reagent. The TNT method is subject to interference from the presence of other polynitroaromatic compounds such as TNB, tetryl and the isomers of DNT. Likewise, the RDX method is interfered with by the presence of other nitramines such as HMX and tetryl, and organonitrate esters such as NG, PETN, and NC. This study investigates the use of thin-layer chromatography (TLC) as a simple on-site method to confirm the identity of analytes detected using colorimetric on-site methods. Separations using both laboratory-grade and locally available solvents were developed. The major limitation of this method is detection capability, which was estimated to be about 0.1 μg of analyte. This corresponds to a concentration of 17 μg/g when using 30 μL of spotting volume, or 500 μg/g when using 1 μL of spotting volume.

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On-Site Analysis of Explosives in Soil

Evaluation of Thin-Layer Chromatography for Confirmation of Analyte Identity

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PREFACE

This report was prepared by Dr. Sae-Im Nam, Research Chemist, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by the U.S. Army Environmental Center (AEC), Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

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SAE-IM NAM

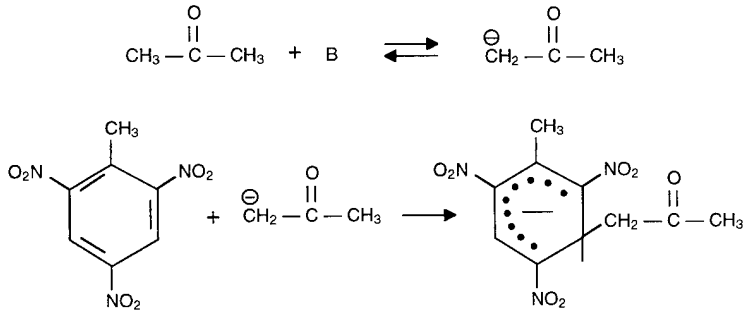
INTRODUCTION

Environmental concerns over explosives contamination in soil have resulted in the determination of the extent of this contamination at numerous Department of Defense installations. Laboratory analytical methods were developed to enable the determination of the most commonly found components of explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and related impurities and environmental transformation products in the soil matrix (Jenkins et al. 1989, U.S. EPA 1995). On-site methods for TNT and RDX, the most commonly encountered contaminants (Walsh et al. 1993), were also developed to provide a more expedient means of rapidly characterizing these sites prior to extensive laboratory analyses (Jenkins and Walsh 1992, Teaney and Hudak 1994). Overall, the use of on-site methods has been successful in providing rapid site characterization at explosives-contaminated sites.

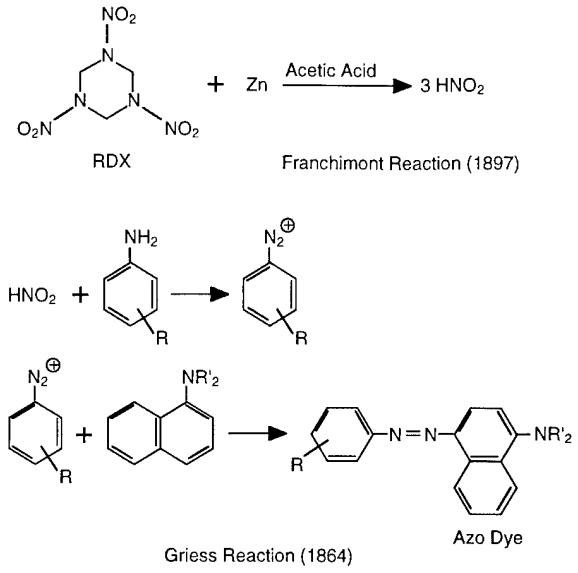
Two of the most commonly used on-site methods for determining the presence of TNT and RDX in soil are based on research conducted at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL). These methods are based on the production of colored products when acetone soil extracts are reacted with the appropriate reagents. In the field screening methods by Jenkins (1990) and Walsh and Jenkins (1991), TNT and RDX, respectively, are converted to color-specific compounds that are quantified spectrophotometrically. Kits containing the associated reagents and supplies are commercially available from EnSys Corporation (now Strategic Diagnostics, Inc., Newark, Delaware). In the TNT method, acetone soil extracts are reacted with strong base as shown in eq 1 to produce reddish-colored Janowsky anions when TNT is present. Reddish-colored anions are also produced, however, when 1,3,5-trinitrobenzene (TNB) or N-methyl-N-2,4,6-tetranitrobenzenamine (tetryl) is present, and a bluish-colored anion is produced when 2,4-dinitrotoluene (2,4-DNT) is present (Jenkins and Walsh 1991). Thus a positive response on the TNT test does not unequivocally prove that TNT is present since several other polynitroaromatics can give a similar response.

For the RDX test, soil extracts are first acidified with acetic acid and reacted with zinc to reduce any RDX present to nitrous acid, and the resulting solution is reacted with a Griess reagent to produce a reddish-colored azo dye (eq 2). Reddish-colored azo dyes are also produced if other nitramines (such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine [HMX] or tetryl) or organonitrate esters (such as nitroglycerin [NG], pentaerythritol tetranitrate [PETN], or nitrocellulose [NC]) are present. In addition, nitrate and nitrite ion, if not removed using an anion exchange column prior to reaction with zinc, will also respond. The ion exchanger is specified in the CRREL-developed method, but is not recommended for routine use by EnSys.

For both of these methods, the intensity of the



Equation 1.



Equation 2.

color is directly proportional to the concentration of the analyte of interest, and concentrations are determined by measuring absorbance at 540 nm for TNT and at 507 nm for RDX. Method detection limits for TNT and RDX in soil samples using these methods are 1.1 µg/g and 1.4 µg/g, respectively.

Often the capability of the TNT test to detect other polynitroaromatics can be quite useful. For example, in a recent study in Sparks, Nevada, areas of contamination with 2,4-DNT were detected using this test (Jenkins et al. 1996). Likewise the capability of the RDX test to determine HMX concentrations was recently demonstrated at an active anti-tank range at Valcartier, Quebec (Jenkins et al. [in press]). As stated previously, these two methods are capable of responding to these TNT- and RDX-related nitroaromatics and nitramines in a like manner. This results in the inability to unequivocally identify which specific compounds are present in many cases without more in-depth laboratory analyses. It is important to be able to discriminate among the various compounds that respond to these tests since cleanup levels for the various explosives can be set at somewhat different concentrations. Therefore it would be quite useful if a simple, inexpensive, on-site method were available to qualitatively determine which of the potentially detectable analytes are giving rise to the colored reaction products from either the TNT or RDX tests.

Thin-layer chromatography (TLC), also known as planar chromatography, is an inexpensive, readily fieldable chromatographic method for separating compounds. As with other chromatographic methods, TLC separations utilize a stationary phase and a mobile phase. The stationary phase is a solid material coated on a glass or plastic plate and the mobile phase is a solvent(s) of variable polarity. Separation is achieved as analytes partition between these phases based on polarity differences as the solvent rises by capillary action through the coated solid. The major advantages of TLC as an on-site method, relative to other chromatographic methods, include the ability to rapidly process a number of samples simultaneously, low capital cost of equipment and supplies, and minimal power requirements.

Brief history of TLC

The earliest development of TLC is attributed to two Russian scientists, Ismailov and Shraiber, in 1938, when they were able to separate certain medicinal compounds on unbound alumina spread on glass sheets (Coker et al. 1993). Their technique was termed "drop chromatography" largely due to the fact that drops of solvent were applied to the plate containing the sample. Then, around 1949, Meinhard and Hall enhanced the method by using binder material to adhere the alumina to the glass plate (Sherma and Fried 1996). However, it was not until 1951 when Kirchner and his colleagues from the U.S. Department of Agriculture further enhanced the method to resemble what is now known as thin-layer chromatography. Kirchner utilized sorbent materials in conjunction with binders on the plates and developed the plates in an ascending fashion, which is commonly used in modern TLC. Then in 1958, Stahl and his colleagues popularized the technique by providing laboratory manuals, which standardized procedures, materials, and nomenclature associated with thin-layer chromatography. By the mid 1960s, instruments such as densitometers were being utilized to quantitatively measure the results of TLC. For the past 30 years continued improvements have been made in the field of thin-layer chromatography, including fully automated instruments that will spot samples, develop plates, analyze the results, and provide quantitative measurements.

Classical TLC was used as early as the mid-1960s to determine components of explosives (DiCarlo et al. 1964, Yasuda 1964, Hoffsommer and McCullough 1968) and more recently, automated multiple development high-performance thin-layer chromatography (AMD-HPTLC) has been used to identify explosives or components of explosives in abiotic matrices such as soil and water

and in a biotic medium such as urine (Yucang et al. 1991, Steuckart et al. 1994). Classical or conventional TLC served to provide more of a qualitative determination of explosives, whereas modern TLC or HPTLC provides both qualitative and quantitative results. The advantage of modern TLC is sensitivity, providing very low limits of detection. However, the initial capital cost of the necessary instrumentation can be high, and usage of highly sensitive equipment is not ideal for field situations unless the equipment is housed in a mobile laboratory. The conventional TLC methods are not as sensitive, but because of very simple equipment requirements, they can be used in the field without significant modifications, at reasonable cost.

Objective

The objective of this work is to evaluate the use of conventional TLC as an adjunct to current on-site colorimetric methods for TNT, RDX, and related compounds. The most popular colorimetric methods often cannot readily distinguish among the various polynitroaromatic compounds that respond to the TNT test, or the various nitramines and nitrate esters that respond to the RDX test. This work evaluates the ability of TLC to separate TNT and the other common polynitroaromatic compounds, and RDX and the other commonly encountered nitramines and nitrate esters in a cost-effective and timely manner.

MATERIALS AND METHODS

Instrumentation and equipment

A basic thin-layer chromatography starter kit was purchased from Alltech Associates, Inc. (Deerfield, Illinois). The starter kit included the following: a 20- × 20-cm TLC tank with glass lid, 20- × 20-cm tank liners, microcap (microcapillary) dispensers (for sample spotting), disposable spray box, spotting template, reagent spray unit with glass jar, and 20- × 20-cm Adsorbosil Plus 1 TLC plates. Additional glass-backed plates consisting of EM silica gel 60 F254 (20 × 20 cm, 250 µm), EM silica gel 60 F254 with preconcentration zone (20 × 20 cm, 250 µm), EM silica gel 60 with preconcentration zone (20 × 20 cm, 250 µm), EM HPTLC silica gel 60 F254 with preconcentrated and prechanneled zones (10 × 10 cm, 200 µm), and Adsorbosil HPTLC with phosphor and preconcentrated zone (10 × 10 cm, 150 µm) were purchased from EM Science, Gibbstown, New Jersey. A multiband (254 and 366 nm) UV lamp with a viewing box was obtained from UVP, Inc., in San Gabriel, California.

Chemicals and reagents

Analytical standards for TNT, TNB, tetryl, 2,4-DNT, 4-A-DNT, 2-A-DNT, RDX, HMX, NG, and PETN were prepared from Standard Analytical Reference Materials (SARM) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland.

Visualizing chemicals and reagents consisting of p-(diethylamino)benzaldehyde (DEAB), p-(dimethylamino)benzaldehyde (DMAB), titanium (III) chloride ($TiCl_3$), ethylenediamine (EDA), potassium permanganate ($KMnO_4$), sodium periodate ($NaIO_4$), diphenylamine (DPA), n-(1-naphthyl)ethylenediamine dihydrochloride and p-(dimethylamino) cinnamaldehyde (DMACA), acetic acid, and zinc were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. TNT EnSys developer reagent was obtained from EnSys, Inc., Research Triangle Park, North Carolina. Potassium hydroxide, hydrochloric acid, hexane, acetonitrile, and sulfanilic acid were purchased from Baker Inc., Phillipsburg, New Jersey. Sodium hydroxide, sodium nitrite, petroleum ether, stoddard solvent, and ethanol were purchased from Fisher Scientifics, Fair Lawn, New Jersey. Butyl alcohol and dimethylsulfoxide (DMSO) were obtained from Mallinckrodt, St. Louis, Missouri. Xylene was furnished by MCB Reagent, Cincinnati, Ohio, and sulfanilamide was from Eastman Kodak Co., Rochester, New York. Acetone and chloroform were from EM Science, Gibbstown, New Jersey, and Burdick & Jackson, Muskegon, Michigan, respectively. Finally, the Hach NitriVer3 powder pillows were from Hach Co., Loveland, Colorado.

Commercial-grade solvents were purchased from local paint and hardware stores. These solvents consisted of Sunnyspec paint thinner, Sterling Lynsol, Sterling Thin-X (red), Sterling VM & P naphtha, Savogram deglosser, Parks VM & P naphtha, Recordsol paint thinner, PPG Industries Duracryl, Sterling acetone, Ace paint thinner, Woolworth-brand 70% isopropanol, Sterling solvent alcohol, and 3M general purpose adhesive cleaner. Mobil gasoline with octane 93 was purchased from a local gas station.

Preparation of visualizing agents

$TiCl_3$ reagent

In a 50-mL volumetric flask, 5 mL of aqueous $TiCl_3$ solution (10% $TiCl_3$ in 20–23% HCl) is combined with 5 mL of 2 N HCl and the solution is

brought to volume with ethanol (Yinon and Zitrin 1981). The solution should be thoroughly mixed and made fresh prior to use.

EDA : DMSO (1 : 1)

A 25-mL portion of EDA is mixed with 25 mL of DMSO. It forms a clear, colorless solution (Hoffsommer and McCullough 1968).

DEAB reagent (0.25% DEAB in 0.25 N HCl in ethanol)

A 250-mg portion of DEAB is mixed with 100 mL of 0.25 N HCl in ethanol until dissolved (Yasuda 1964). The resulting solution is yellow-orange in color and may be stored in the dark at 4°C for up to three weeks.

DMAB reagent

A 1-g portion of DMAB is mixed with 3 mL of HCl, 30 mL of ethanol, and 18 mL of butanol. The resulting solution is light yellow in color and may be stored in the dark at 4°C for up to three weeks (Jork et al. 1994b).

Bratton-Marshall reagent

A 0.1-g portion of N-1-naphthylethylenediamine•2 HCl is mixed with 5 mL of 2 N HCl and 95 mL of butanol (Yinon and Zitrin 1981). The solution is stirred until dissolved. The resulting solution is light gray in color.

DMACA reagent (0.25% DMACA in 0.25 N HCl in ethanol)

A 250-mg portion of DMACA is mixed with 100 mL of 0.25 N HCl in ethanol until dissolved (Jork et al. 1994b). The resulting solution is yellow-orange in color and may be stored in the dark at 4°C for up to three weeks.

$NaIO_4$ and $KMnO_4$ reagent (0.1% $NaIO_4$ and 0.5% $KMnO_4$ in 4% NaOH)

A 0.1-g portion of $NaIO_4$ is combined with 0.5 g of $KMnO_4$, and 100 mL of 4% NaOH is added and mixed until dissolved (Carlson and Thompson 1986).

1% DPA

A 500-mg portion of DPA is dissolved in 50 ml of ethanol (Bagnato and Grasso 1986).

$NaNO_2$

A 0.5-g portion of sodium nitrite is dissolved in 10 mL of water and the solution is brought to 50 mL with an ethanol and HCl mixture (41.5 mL of ethanol and 8.5 mL of HCl) (Jork et al. 1994b).

5% KOH

A 5-g portion of KOH is dissolved in 100 mL of ethanol (Jork et al. 1994a).

Hach NitriVer3 solution

Two packets of prepackaged Hach NitriVer3 powder pillows are dissolved in 40 mL of water (Walsh and Jenkins 1991).

Griess reagents

Peak's Griess reagent (Peak 1980). Solution A: A 0.1-g portion of N-1-naphthylenediamine dichloride is dissolved in 100 mL of water.

Solution B: A 0.5-g portion of sulfanilic acid is dissolved in 14 mL of acetic acid and brought to 100 mL with water. Equal amounts of solutions A and B are added together immediately before use. Individual solutions may be stored in the dark at 4°C for up to three weeks.

Higg's Griess reagent (Higgs and Hayes 1982). Solution A: A 20-mg portion of N-1-naphthylethylenediamine dichloride is dissolved in 100 mL of 0.1 N HCl.

Solution B: A 200-mg portion of sulfanilic acid is dissolved in 100 mL of 2 N HCl. Equal volumes of both solutions are mixed together immediately before use.

Preparation of standards and sample extracts

Stock standard solutions of TNT (1000 mg/L), TNB (725 mg/L), tetryl (505 mg/L), 2,4-DNT (1000 mg/L), 2-A-DNT (1000 mg/L), 4-A-DNT (1000 mg/L), RDX (1000 mg/L), HMX (1000 mg/L), PETN (2000 mg/L), and NG (2000 mg/L) were prepared by dissolving the dry material in either HPLC-grade acetone or acetonitrile. The stock solutions were further diluted when smaller concentrations were needed. Soil samples used in this study were previously obtained from Defence Research Establishment Valcartier (DREV) Tank Firing Range in Quebec, Canada; Hawthorne Ammunition Plant in Nevada; Savanna Army Depot in Illinois; and Umatilla Army Depot in Oregon. Soil extracts were prepared as described by Jenkins (1990) and Walsh and Jenkins (1991).

General thin-layer chromatography procedures

The developing tank was prepared by the addition of the mobile phase (200 mL) and equilibrated for approximately 30 to 40 minutes or until the tank liner had been saturated. The TLC plates were prepared for sample spotting by designating the

line of origin (about 2–3 cm above the bottom of the plate) and the solvent front line (10 cm from the line of origin). Using capillary micropipettes, samples were spotted along the line of origin approximately 1 cm apart. Spotting volumes ranged from 0.5 to 30 µL, but in most cases, samples were spotted 1 µL at a time. The plates were then placed in the developing tank (containing the freshly prepared mobile phase) and developed in an ascending manner until the mobile phase had reached the solvent front line. The plates were removed from the tank and either air dried or dried with hot air from a heat gun prior to observation. The fluorescence-containing plates were observed under the UV lamp (set at 254 nm) and/or sprayed with visualizing agents. Nonfluorescence-containing plates were sprayed with visualizing agents. The position of the resulting nonfluorescing spots (observed under the UV light) or colored spots was marked and the retention factor (Rf) values were determined by dividing the distance traveled by the compound by the distance traveled by the solvent front. When analyzing soil samples, analytes were identified by comparing the Rf values to the Rf values of the standards that were spotted on the same plate.

RESULTS AND DISCUSSION

Separation of nitroaromatics using laboratory-grade and commercial-grade solvents

Numerous mobile phase systems were tested to determine the best solvent or combination of solvents that would result in a distinguishable separation of nitroaromatic compounds such as TNT, TNB, DNT, tetryl, and the isomers of amino-DNTs. The evaluated mobile phase systems using laboratory-grade solvents included hexane : chloroform (4 : 1), chloroform, petroleum ether : acetone (3 : 1) and (2 : 1), petroleum ether : isopropanol (4 : 1), xylene, and Stoddard solution : isopropanol (2 : 1) and (1 : 1). These solvents were chosen according to their eluting strength. The combination of four parts petroleum ether with one part isopropanol resulted in the best distinguishable separation of nitroaromatic compounds compared to the other evaluated mobile phase systems (Table 1). The solvent system of hexane : chloroform (4 : 1) resulted in no movement of the compounds. Chloroform, by itself, resulted in identifiable separation of TNT, TNB, DNT, and tetryl, but the Rf values of the amino-DNTs were nearly identical. The combination solvents of petroleum ether and acetone at various ratios also failed to separate the compounds efficiently. Xylene, by itself, and Stoddard solution (a clear petroleum distillate) with isopropanol were fairly effective in separating the nitroaromatic compounds, but their development times were considerably longer compared to the other laboratory-grade solvent systems (Table 2).

Commercial-grade paint thinners and alcohols, which are readily available in any local hardware or paint store, were also evaluated for their ability to separate nitroaromatic compounds. However, because of the high water content in commercially available alcohols (i.e., Woolworth-brand 70% isopropanol and Sterling solvent alcohol), all mobile

Table 1. Separation of nitroaromatics with laboratory-grade solvents.

Solvent systems	*TNT Rf ± S.D.*	*TNB Rf ± S.D.*	*2,4-DNT Rf ± S.D.*	*Tetryl Rf ± S.D.*	*2-A-DNT Rf ± S.D.*	*4-A-DNT Rf ± S.D.*
1	0.52	0.36	0.48	0.20	0.16	0.14
2	0.42	0.40	0.40	0.27	0.22	0.23
3	0.47	0.46	0.45	0.33	0.30	0.30
4	0.64 ± 0.02	0.58 ± 0.02	0.52 ± 0.02	0.37 ± 0.02	0.23 ± 0.02	0.27 ± 0.02
5	0.75	0.71	0.63	0.62	0.55	0.55
6	0.74	0.72	0.65	0.67	0.62	0.62
7	0.54	0.50	0.47	0.28	0.1	

Solvent system key:
1—Chloroform
2—Petroleum ether : acetone (3 : 1)
3—Petroleum ether : acetone (2 : 1)
4—Petroleum ether : isopropanol (4 : 1), $n = 3$
5—Stoddard solution : isopropanol (2 : 1)
6—Stoddard solution : isopropanol (1 : 1)
7—Xylene

Table 2. Development times.

Solvent system	*Time (min.)*
Stoddard solution : isopropanol (2 : 1) and (1 : 1)	50
Chloroform	10
Petroleum ether : acetone (3 : 1) and (2 : 1)	16
Petroleum ether : isopropanol (4 : 1)	17
Xylene	25
3M adhesive cleaner : isopropanol (4 : 1)	24
Duracryl : isopropanol (4 : 1)	26
Deglosser : isopropanol (4 : 1)	44
Recorder paint thinner : isopropanol (4 : 1)	46
Parks VM & P naphtha : isopropanol (4 : 1)	30
Sterling VM & P naphtha : isopropanol (4 : 1)	23
Sterling Thin-X paint thinner : isopropanol (4 : 1)	50
Ace paint thinner : isopropanol (4 : 1)	45

phases prepared with these alcohols resulted in very little or no movement of the nitroaromatic compounds. However, when commercially available paint thinners were mixed with laboratory-grade isopropanol (4 : 1), compounds such as TNT, DNT, TNB, and tetryl could be distinguished from each other (Table 3). Commercial brands such as Recorder paint thinner, Sterling VM & P naphtha, Sterling Thin-X paint thinner, and Ace paint thinner were among the tested brands that have resulted in good-to-fair separation of TNT, DNT, TNB, and tetryl. However, in most cases, the development time took longer than when the mobile phase was composed solely of laboratory-grade solvents (Table 2).

Separation of nitramines and nitrate esters using laboratory-grade and commercial-grade solvents

The solvent system of petroleum ether and acetone (1 : 1) was found to be very effective in separating the nitramines, such as RDX and HMX, and to produce a fair separation of the nitrate esters, PETN and NG (Table 4). RDX, PETN, and NG were also effectively separated with petroleum ether : isopropanol (4 : 1), but HMX failed to move from the line of origin.

Mobile-phase solvents consisting of commercial-brand acetone and some paint thinners (1 : 1) were also effective in producing a good separation of RDX and HMX (Table 5). However, the separation of PETN and NG was not as clear, thus resulting in very similar Rf values.

Evaluation of TLC plates

TLC plates used in this study were all glass plates precoated with silica gel. The differing features of these plates included different commercial brands, fluorescence vs. nonfluorescence, and preconcentration zone vs. no preconcentration zone. The preconcentration area, located on the bottom of the plate, is made up of inert material that is meant to absorb sample solvent. The two brands of TLC plates, EM and Adsorbosil, did not show any significant differences regarding separation of analytes. When using the same solvent system and visualizing procedures, both plates were nearly identical in results with slight color

Table 3. Separation of nitroaromatic compounds with commercial-brand paint thinners and laboratory-grade isopropanol (4 : 1).

Solvent systems	*TNT Rf ± S.D.*	*TNB Rf ± S.D.*	*2,4-DNT Rf ± S.D.*	*Tetryl Rf ± S.D.*	*2-A-DNT Rf ± S.D.*	*4-A-DNT Rf ± S.D.*
1	0.78 ± 0.04	0.76 ± 0.04	0.65	0.68 ± 0.05	0.54 ± 0.01	0.56 ± 0.01
2	0.88 ± 0.02	0.88 ± 0.01	0.86 ± 0.01	0.85 ± 0	0.83 ± 0.01	0.84 ± 0.01
3	0.74 ± 0.01	0.69 ± 0.02	0.71	0.65 ± 0.04	0.59 ± 0.04	0.61 ± 0.04
4	0.70 ± 0.07	0.67 ± 0.05	0.61 ± 0.04	0.52 ± 0.04	0.39 ± 0.01	0.43 ± 0.04
5	0.72 ± 0.02	0.68 ± 0	0.63 ± 0.01	0.57 ± 0.02	0.40 ± 0.01	0.43 ± 0
6	0.65 ± 0.00	0.60 ± 0	0.55 ± 0	0.48	0.35	0.40
7	0.74 ± 0.01	0.68 ± 0	0.64 ± 0.01	0.53 ± 0	0.42 ± 0.02	0.44 ± 0
8	0.79 ± 0.01	0.76 ± 0.02	0.66 ± 0.01	0.62 ± 0.02	0.45 ± 0.01	0.49 ± 0.02

Solvent system key:
1—3M adhesive cleaner : isopropanol, $n = 2$
2—Duracryl : isopropanol, $n = 2$
3—Deglosser : isopropanol, $n = 2$
4—Recorder paint thinner : isopropanol, $n = 2$
5—Parks VM & P naphtha : isopropanol, $n = 2$
6—Sterling VM & P naphtha : isopropanol, $n = 2$
7—Sterling Thin-X paint thinner : isopropanol, $n = 2$
8—Ace paint thinner : isopropanol, $n = 3$

Table 4. Separation of nitramines and nitrate esters with laboratory-grade solvents.

Solvent systems	n	RDX Rf ± S.D.	HMX Rf ± S.D.	PETN Rf ± S.D.	NG Rf ± S.D.
Petroleum ether : acetone (1 : 1)	3	0.72 ± 0.01	0.62 ± 0.01	0.91 ± 0.03	0.88 ± 0.02
Petroleum ether : isopropanol (4 : 1)	3	0.30 ± 0.02	No movement	0.84 ± 0.03	0.79 ± 0.02

intensity variations. The fluorescent and nonfluorescent plates were found to produce identical separations. However, the plates having preconcentration zones did give better analyte resolution, compared to plates having no preconcentration zones, when the spotting volume exceeded 5 µL. This result was in agreement with Rabel and Palmer (1992) and Hauck and Mack (1990), in which they report enhanced resolution, reproducibility, and recovery of analytes spotted on preconcentration zones.

Evaluation of HPTLC plates

According to Fenimore and Davis (1981), when high-performance thin layer chromatography (HPTLC) plates are used in conjunction with modern scanning equipment, the limit of detection can be similar to those obtained by high-performance liquid chromatography (HPLC). HPTLC plates, like conventional TLC plates, are usually coated with various binders to hold sorbent material together. However, the dimensions of HPTLC plates are approximately half the size of conventional plates. The particle sizes of the sorbent material are much smaller and the size distribution of these particles is much tighter. HPTLC plates are also thinner and the surface is more uniform than conventional plates. These differences often can result in use of smaller sample volume, smaller solvent volume for the mobile phase, shorter solvent migration distance, and greater sensitivity for the detection of separated compounds.

HPTLC plates were evaluated here to determine if the separation and resolution of compounds were better relative to standard TLC plates when using conventional techniques. Two different brands of HPTLC plates were evaluated (EM and Adsorbosil). Both brands had preconcentration zones, with the EM plates also having channeled zones while the Adsorbosil did not. The compounds were spotted along the preconcentration zone using microcapillary dispensers. Because of the size of the plates (10 × 10 cm) and thinner thickness (150–200 µm), the developing time was usually between 10 and 15 minutes, half the development time of standard TLC plates. The HPTLC plates also required less mobile phase volume compared to standard TLC plates. However, when the compounds were visualized with UV light or with visualizing agents, the separation and resolution of compounds, including nitroaromatics, nitramines, and nitrate esters, were similar to the standard TLC plates (Table 6). The two brands of HPTLC plates behaved similarly and results showed no difference in separation and resolution of compounds between plates having channeled zones and no channeled zones.

Evaluation of visualizing agents

Numerous visualizing agents as well as UV light were evaluated for their effectiveness in visualizing components of explosives. In most cases, the evaluated visualizing agents were chosen in accordance with the literature. The summary of the

Table 5. Separation of nitramines and nitrate esters with commercial-brand solvents.

Solvent systems	RDX Rf ± S.D.	HMX Rf ± S.D.	PETN Rf ± S.D.	NG Rf ± S.D.
3M adhesive cleaner : Sterling acetone (1 : 1)*	0.58 ± 0.04	0.53 ± 0.04	0.80 ± 0.05	0.78
Parks VM & P naphtha: Sterling acetone (1 : 1)*	0.54 ± 0.01	0.45 ± 0.03	0.73 ± 0.05	0.69 ± 0.06
Sterling VM & P naphtha: Sterling acetone (1 : 1)*	0.53 ± 0.01	0.42 ± 0.02	0.65 ± 0.06	0.63 ± 0.04
Sterling Thin-X : Sterling acetone (1 : 1)**	0.53 ± 0.03	0.43 ± 0.08	0.59 ± 0.03	0.60 ± 0.03
Ace paint thinner : Sterling acetone (1 : 1)*	0.48 ± 0.07	0.36 ± 0.09	0.61 ± 0.04	0.59 ± 0.05

*$n = 2$
**$n = 3$

Table 6. Comparison of HPTLC plates and TLC plates.

	Petroleum ether : isopropanol (4 : 1)		*Petroleum ether : acetone (1 : 1)*	
Compounds	*HPTLC Rf* ± S.D.*	*TLC Rf* ± S.D.*	*HPTLC Rf* ± S.D.*	*TLC Rf* ± S.D.*
TNT	0.83 ± 0.03	0.64 ± 0.02		
TNB	0.79 ± 0.02	0.58 ± 0.02		
2,4-DNT	0.73 ± 0.03	0.52 ± 0.02		
Tetryl	0.68 ± 0.01	0.37 ± 0.02		
2-A-DNT	0.57 ± 0.00	0.23 ± 0.02		
4-A-DNT	0.62 ± 0.02	0.27 ± 0.02		
RDX	0.32 ± 0.02	0.30 ± 0.02	0.65 ± 0.05	0.72 ± 0.01
HMX	No movement	No movement	0.57 ± 0.06	0.62 ± 0.01
PETN	0.82 ± 0.02	0.84 ± 0.03	0.82 ± 0.04	0.91 ± 0.03
NG	0.75 ± 0.02	0.79 ± 0.02	0.79 ± 0.04	0.88 ± 0.02

*$n = 3$

results is shown in Table 7. In most cases, the evaluated visualizing agents worked well in visualizing nitroaromatic compounds, but were fairly limited in visualizing nitramines and nitrate esters.

UV light and EnSys TNT developer

The simplest method for visualizing nitroaromatics and nitramines was viewing the developed plate under shortwave (254 nm) UV light (Glover and Hoffsommer 1973, McCormick et al. 1978, Malotky and Downes 1983, and Zou et al. 1994). We found the fluorescence-containing plates to have bright green backgrounds with light-to-dark spots representing nitroaromatic and nitramine compounds. Following the UV viewing, nitroaromatics could be further distinguished by placing approximately 1 µL of the EnSys TNT developer on the dark spots. The EnSys TNT developer reacts with the nitroaromatic compounds to form Meisenheimer complexes and results in the following color formations: purple for TNT, orange for tetryl, light yellow for 4-A-DNT, orange for TNB, light yellow for 2-A-DNT, and light green for 2,4-DNT. The intensity of the color varied depending on the concentration of the compound.

$TiCl_3$ and DEAB, $TiCl_3$ and DMAB, and $TiCl_3$ and DMACA

These three visualizing agents worked well in visualizing nitroaromatic compounds. They are grouped together due to similar reaction principle (Yasuda 1964, 1970, Yinon and Zitrin 1981, and Jork et al. 1994b). The developed plates are initially sprayed with the $TiCl_3$ reagent, which reduces the nitroaromatic compounds to amines. When the plate is dried, it is sprayed with either DEAB, DMAB, or DMACA, which react with the amines to form Schiff bases. Compounds sprayed with DEAB resulted in yellow-colored products, DMAB-sprayed compounds were orange-yellow in color, and compounds sprayed with DMACA resulted in purple colors. The color developments were immediate after the application of DEAB, DMAB, or DMACA and were best viewed when the plate was still wet.

EDA : DMSO

The solution of EDA : DMSO (1 : 1) reacts with nitroaromatic compounds to form Meisenheimer complexes. The results we obtained were similar to Hoffsommer and McCullough (1968). Upon spraying the plate with EDA : DMSO solution, the resulting colors were purple for TNT, orange for tetryl, red-orange for TNB, faint yellow for 2-A-DNT, and light green for 2,4-DNT (while the plate was still wet).

Alkaline solution (5% KOH, 1 N NaOH, 0.1 N NaOH) and Griess reagent, 5% KOH and Bratton-Marshall reagent, and 5% KOH and Hach NitriVer3

These visualizing agents behave similarly in that their reactions all follow a similar principle. The alkaline solution is initially used to reduce the compounds to form nitrite ions. These ions are then converted to azo compounds in the acidic medium and coupled to naphthalene derivatives (which are found in the Griess reagent, the Bratton-Marshall reagent, and the Hach NitriVer3) to form the characteristic colors. Slight variations in the formulation of the Griess reagent resulted in different color formation (Table 7). According to the literature, nitrate esters and nitramines reacting

Table 7. Visualization of nitroaromatics, nitramines, and nitrate esters.

Visualizing agent	*Visualized compounds**	
Ensys TNT developer	• TNT- purple • Tetryl- orange	• TNB- orange • DNT- light green after acetone
$TiCl_3$ and DMAB	• TNT- orange yellow • Tetryl- light brown • 4-A-DNT- golden yellow	• TNB- orange yellow • 2-A-DNT- light orange yellow • DNT- light orange yellow
$TiCl_3$ and DEAB	• TNT- bright yellow • Tetryl- light yellow • 4-A-DNT- yellow	• TNB- orange-yellow • 2-A-DNT- yellow • DNT- yellow
$TiCl_3$ and DMACA	• TNT- pinkish purple • Tetryl- purple • 4-A-DNT- purple	• TNB- purple • 2-A-DNT- purple • DNT- light purple
$TiCl_3$, $NaNO_2$, and Bratton-Marshall	• TNT- purple • Tetryl- light pink • 4-A-DNT- purple	• TNB- purplish pink • 2-A-DNT- purple • DNT- purple
EDA : DMSO (1:1)	• TNT- purple • Tetryl- orange • TNB- red-orange	• 2-A-DNT- faint yellow • DNT- faint light green when the plate is wet
5% KOH and Hach NitriVer3	• TNT- peachy orange • Tetryl- light yellow	• TNB- light pink • 2-A-DNT- light yellow
5% KOH and modified Griess reagent	• TNT- light purple • Tetryl- light purple	• TNB- light purple
5% KOH and Bratton-Marshall reagent	• TNT- faint light purple • Tetryl- faint light purple	• TNB- faint light purple
0.1 NaOH and Peak's Griess reagent	• Tetryl- very faint yellow • 2-A-DNT- faint yellow	• NG- pink
1 NaOH and Higg's Griess reagent	• RDX- light reddish brown • TNT- reddish brown • Tetryl- light yellow	• 2-A-DNT-very light yellow • NG- purplish pink
5% KOH and Higg's Griess reagent	• TNT- peach • Tetryl- yellow • TNB- faint pink	• 2-A-DNT- light yellow • NG- pink
5% KOH and Hach NitriVer3	• TNT- peachy-brown • Tetryl- light yellow	• TNB- light pink • 2-A-DNT- light yellow
$NaIO_4/KMnO_4$ spray	• TNT- yellow • Tetryl- light yellow • TNB- light yellow	• 2-A-DNT- light yellow • DNT- light yellow
5% EDA in ethanol	• TNT- light brown • Tetryl- peachy brown	• TNB- light orange • 2-A-DNT- light, light yellow
Griess reagent and UV exposure for 30 min. followed by heat drying	• PETN- lime green • NG- lime green	• RDX- light blue • HMX- light blue
1% or 5% DPA and UV exposure for 15 min.	• PETN- olive green • NG- olive green	• RDX- light purple

*Spotted 1 μg of compound.

with Griess reagents yielded colors that characterize these compounds, but in most cases we found nitroaromatic compounds to be more visible with the exception of 2,4-DNT and 4-A-DNT. Griess reagent formulation by Peak and Higgs resulted in a pinkish color for NG. The Hach NitriVer3, when used in conjunction with acidified zinc, detects RDX from soil and groundwater extracts (Walsh and Jenkins 1991, Jenkins et al. 1994), but Hach NitriVer3 used in conjunction with 5% KOH did not yield any color formation for nitrate esters (PETN and NG) nor for nitramines (RDX and HMX). The absence of color(s) may have been due to the omission of an acidic environment. When using the visualizing agents in this category the best viewing of colors was after the plates had completely dried.

$NaIO_4/KMnO_4$

According to Carlson and Thompson (1986), sodium metaperiodate (0.1%) and potassium permanganate (0.5%) in a 4% sodium hydroxide solution yields yellow spots for NG on a dry plate and green spots for PETN on a wet plate, all against a violet background. DiCarlo et al. (1964) also observed similar results for PETN when sprayed with a solution containing 4 : 1 : 1 of sodium metaperiodate (2%) : potassium permanganate (1%) : sodium bicarbonate (2%). However, our results yielded no color formation for nitrate esters. Some nitroaromatics developed yellow spots after the plate had been dried in a 100°C oven for five minutes (Table 7). The failure to observe the nitrate esters may partly be due to spotting of lower levels of NG and PETN (1 to 2 µg) compared to the literature values of 2 to 25 µg.

1% or 5% DPA and UV exposure

DiCarlo et al. (1964), Parker et al. (1975), and Bagnato and Grasso (1986) all report color visualization of PETN with either 1% or 5% DPA followed by UV light exposure. Parker et al. (1975) also included NG and RDX while Bagnato and Grasso (1986) were able to also observe HMX. The results we obtained were similar. PETN and NG appeared green–gray and RDX was light pinkish–purple.

Griess reagent and UV exposure

Spraying with Griess reagent followed by UV light exposure for approximately 30 minutes resulted in pink-colored spots for RDX, HMX, PETN, and NG. However, when the plates were dried in a 110°C oven for 20 minutes, RDX and HMX yielded light blue spots while PETN and NG had lime green spots.

Estimation of detection capability

A preliminary estimation of the minimum detectable level for each explosive was determined by spotting different volumes (ranging from 0.5 to 30 µL) of each standard solution. The concentration of the various standard solutions ranged from 5 to 2000 mg/L. Depending on the analyte of interest, UV viewing and visualizing agents were employed to visualize (or detect) the intended compound. Table 8 lists the lowest detectable quantity that could be visualized for each explosive. All analytes were visible at 1-µg quantity either by UV viewing or by spraying with a visualizing agent. In samples containing high concentration of analyte (>1000 mg/L), a spotting volume of 1 µL was sufficient to allow visualization of the analyte, but in samples containing lower levels (<100 mg/L), the spotting volumes could be as high as 30 µL (on a preconcentration zone) without causing streaking or too much spreading of the analyte. TNT and TNB were the only analytes that were consistently visualized at 0.1-µg quantity, which was equivalent to a spotting volume of 10 µL of standard solution of 10 mg/L or 1 µL of 100 mg/L. The remaining nitroaromatics were also visible at 0.1-µg quantity when sprayed with $TiCl_3$ and DMACA; however, more tests are needed to fully assess the reliability of detection at this level. RDX was also visualized at 0.1-µg quantity under UV viewing, but the observations were more consistent with HPTLC plates than with conventional plates. While the HPTLC plates did not play a role in significantly enhancing the separation of analytes, with regard to detection capabilities, the properties of HPTLC plates seemed to enhance the detectability of nitramines and nitrate esters.

Testing of soil samples collected from the field

Soil samples collected from the field (ranging from ammunition plants to firing ranges) were analyzed using the conventional TLC methods to determine or confirm the accuracy of its separation procedures. The concentration of the analytes from these soil samples was previously determined by standard HPLC methods. In most cases, soil samples were extracted with acetone (1 to 5 ratio) and the filtered extracts were spotted on TLC plates. Soil from Umatilla Army Depot, which contained 716 µg of TNT per gram of soil, was extracted and spotted (10 × 1 µL). This yielded a vis-

Table 8. Lowest level of visualization.

Compound	*Lowest level (μg)*	*Visualizing agent*	*Frequency*
Nitroaromatics: TNT	0.1	UV exposure	4/4
		$TiCl_3$ and DMACA	8/8
		EDA : DMSO (1 : 1)	1/1
		HPTLC*/UV exposure	4/4
		HPTLC*/$TiCl_3$ and DMACA	1/1
		HPTLC*/EDA : DMSO (1 : 1)	3/3
Tetryl	0.01	$TiCl_3$ and DMACA	1/1
	0.05	EDA : DMSO (1 : 1)	1/1
		HPTLC*/$TiCl_3$ and DMACA	1/1
		HPTLC*/EDA : DMSO (1 : 1)	2/2
TNB	0.1	UV exposure	4/4
		$TiCl_3$ and DMACA	8/8
		HPTLC*/UV exposure	3/3
		HPTLC*/EDA : DMSO (1 : 1)	2/2
4-A-DNT	0.1	UV exposure	1/1
		$TiCl_3$ and DMACA	1/1
2-A-DNT	0.1	UV exposure	3/3
		$TiCl_3$ and DMACA	1/1
2,4-DNT	0.1	UV exposure	3/4
		$TiCl_3$ and DMACA	6/6
		HPTLC*/$TiCl_3$ and DMACA	1/1
Nitramines: RDX	0.1	UV exposure	4/7
		Griess and UV exposure	1/1
		HPTLC*/UV exposure	8/8
		HPTLC*/5% DPA and UV exposure	1/5
HMX	0.1	HPTLC*/UV exposure	3/3
	0.2	Griess and UV exposure	2/2
Nitrate esters: PETN	0.2	HPTLC*/1% DPA and UV exposure	1/1
	0.4	Griess and UV exposure	2/2
NG	0.2	HPTLC*/1% DPA and UV exposure	1/1
	0.4	Griess and UV exposure	2/2

*High-performance thin-layer chromatography plates.

ible spot under UV light that corresponded to the same Rf value as the spot from a standard solution of TNT. A soil sample from Hawthorne Ammunition Plant containing an array of explosives, including HMX (2.4 mg/g), RDX (8.1 mg/g), TNB (0.088 mg/g), DNB (0.002 mg/g), TNT (13.9 mg/g), and 2,4-DNT (0.007 mg/g), was extracted. When 1 μL of the extract was spotted and developed, two spots that corresponded to TNT and RDX were visible under UV light. Soil collected from DREV had tested positive for RDX using the RDX field screening kit (Walsh and Jenkins 1991), but the explosive most commonly used in that area was HMX. When 10 μL of the DREV soil extract was spotted and developed using the solvent system of petroleum ether : acetone (1 : 1), a single pink spot appeared after spraying the plate with Griess reagent and exposing the plate under UV light for 30 minutes. When the Rf value for the spot from the DREV sample was compared to the Rf values of the standard RDX, HMX, PETN, and NG, it corresponded to HMX, and the identity was confirmed by standard HPLC methods. In most cases, soil samples collected from the field contained a high concentration of TNT with very low levels of other nitroaromatics. When soil extracts from these samples were spotted, because of the high TNT concentration, other nitroaromatics could not clearly be identified. To determine the effectiveness of the TLC method in separating nitroaromatic compounds in extracts from field samples, soil from Savanna Army Depot, which

contained similar levels of TNT (14 µg/g) and TNB (9.4 µg/g), was used. Soil samples were extracted in acetone as described above, but to maximize the extract concentration, the soil-to-solvent ratio was increased to 1 : 2 (1 gm of soil to 2 mL of acetone). A volume of 20 µL (which was equivalent to 0.14 µg of TNT and 0.094 µg of TNB) was spotted and developed in the solvent system of Sterling VM & P naphtha and laboratory-grade isopropanol (4 : 1). Plates were sprayed with $TiCl_3$, $NaNO_2$, and Bratton-Marshall reagent (Jork et al. 1994b). Two spots, light purple in color, were identified as TNT and TNB. These results seemed to indicate that TLC could be used to separate and distinguish different explosives components in actual field samples when appropriate solvent system and visualizing procedures are utilized.

Recommendations for specific separations and visualizing reagents

The solvent system of petroleum ether and isopropanol (4 : 1) is recommended to separate various species of nitroaromatic compounds, including TNT, TNB, and DNT. The most sensitive visualizing agents tested for nitroaromatics are $TiCl_3$ followed by DMACA spray. For the separation of nitramines such as RDX and HMX, and nitrate esters PETN and NG, the solvent system of petroleum ether and acetone (1 : 1) is recommended with visualization with Griess reagent followed by UV exposure. Optimal separation occurs with laboratory-grade solvents; however, in cases where laboratory-grade solvents are not readily available, commercially available solvents such as paint thinner and acetone may be substituted. If sensitivity is not an issue, commercially available solvents will be more cost-effective and more readily available in the field.

CONCLUSIONS

For the purposes of this evaluation, the conventional TLC approach was used rather than the modern TLC techniques for the following reasons: 1) the conventional TLC techniques involve less equipment, and so are less expensive and are field portable, and 2) the purpose of this report was to evaluate a method that can be used in conjunction with on-site colorimetric methods. The results indicate TLC methods could indeed be used to separate various components of explosives such as TNT, TNB, DNT, RDX, HMX, PETN, and NG from soil samples. Using appropriate solvent systems such as petroleum ether and isopropanol (4 : 1) and petroleum ether and acetone (1 : 1), nitroaromatic, nitramine, and nitrate ester compounds could be effectively separated. In most cases, commercial-brand solvents (which are readily available in hardware stores) were also effective in giving good-to-fair separation of components of explosives. However, as mentioned at the onset of this report, the detection capability of conventional TLC methods is poor, and this remains the major limitation of this method. The conventional TLC method evaluated in this report is capable of detecting 0.1 µg of TNT or RDX with either UV, $TiCl_3$ spray followed by DMACA, or Griess reagent followed by UV exposure. This is equivalent to spotting a volume of 1 µL of sample extract containing 100 µg/mL of TNT or RDX, and if the sample extract was prepared using the soil-to-solvent ratio used in the on-site colorimetric methods (20 g of soil to 100 mL of acetone), the concentration of TNT or RDX in soil would correspond to approximately 500 µg/g. This is about 500 times above the minimum detection limit for TNT (1.1 µg/g) and RDX (1.4 µg/g) colorimetric on-site tests. Even if the maximum spotting volume of 30 µL is used, the detection capability remains at about 17 µg/g if the soil-to-solvent ratio is maintained at 20 g and 100 mL. If a larger soil-to-solvent ratio is used to obtain an extract for TLC analysis, the detection capability could be further improved. More experiments aimed at optimizing detection capability by either concentrating sample extracts and/or utilizing higher soil-to-solvent ratios are needed to fully assess the practical limit of detection for the TLC method.

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13. ABSTRACT (*Maximum 200 words*)

Two colorimetric-based methods are commonly used for on-site analysis of explosives in soil. For the TNT method, acetone soil extracts are reacted with base to produce reddish-colored Janowsky ions. For RDX, acetone extracts are acidified and reacted with zinc to reduce RDX to nitrous acid, and the nitrous acid is determined by reacting the resulting solution with a Griess reagent. The TNT method is subject to interference from the presence of other polynitroaromatic compounds such as TNB, tetryl, and the isomers of DNT. Likewise, the RDX method is interfered with by the presence of other nitramines such as HMX and tetryl, and organonitrate esters such as NG, PETN, and NC. This study investigates the use of thin-layer chromatography (TLC) as a simple on-site method to confirm the identity of analytes detected using colorimetric on-site methods. Separations using both laboratory-grade and locally available solvents were developed. The major limitation of this method is detection capability, which was estimated to be about 0.1 μg of analyte. This corresponds to a concentration of 17 μg/g when using 30 μL of spotting volume, or 500 μg/g when using 1 μL of spotting volume.

14. SUBJECT TERMS
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